PESTICIDE SURFACE WATER AND SEDIMENT QUALITY REPORT

MAY 2003 SAMPLING EVENT



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Pesticide Monitoring Project Report May 2003 Sampling Event

Summary

As part of the District's quarterly ambient monitoring program, unfiltered water and sediment samples from 39 sites were collected from May 11 to May 14, 2003, and analyzed for over sixty pesticides and/or products of their degradation. The herbicides 2,4-D, ametryn, atrazine, bromacil, diuron, hexazinone, metolachlor, norflurazon, prometon, and simazine, along with the insecticides/degradates atrazine desethyl, atrazine desisopropyl, and endosulfan sulfate were detected in one or more of these surface water samples.

The herbicides ametryn, atrazine, bromacil, and norflurazon together with the insecticides/degradates DDD, DDE, DDT, ethion, and one PCB compound were found in the sediment at several locations. One DDD and four DDE compound sediment concentrations were of a magnitude considered to have a harmful effect on freshwater sediment-dwelling organisms.

The compounds and concentrations found are typical of those expected from intensive agricultural activity.

Background and Methods

The District's pesticide monitoring network includes stations designated in the Everglades National Park Memorandum of Agreement, the Miccosukee Tribe Memorandum of Agreement, the Lake Okeechobee Operating Permit, and the non-Everglades Construction Project (non-ECP) permit. The District's canals and marshes depicted in Figure 1 are protected as Class III (fishable and swimable) waters, while Lake Okeechobee is protected as a Class I drinking water supply. Water Conservation Area 1 (WCA1) and the Everglades National Park are also designated as Outstanding Florida Waters, to which anti-degradation standards apply. Surface water and sediment are sampled quarterly and semiannually, respectively, upstream at each structure identified in the permit or agreement.

Sixty-six pesticides and degradation products were analyzed for in samples from all of the 39 sites (Figure 1). The analytes, their respective minimum detection limits (MDL), and practical quantitation limits (PQL) are listed in Table 1. All the analytical work is performed by the Florida Department of Environmental Protection (FDEP) Central Laboratory in Tallahassee Florida. The reader is referred to the *Quality Assurance Evaluation* section of this report for a summary of any limitations on data validity that might influence the utility of these data.

Each pesticide's description and possible uses and sites of application are taken from Hartley and Kidd (1987). The Florida Ground Water Guidance Concentrations (FGWGC) (FDEP, 1994) are listed to provide an indication at what level these pesticide residues could possibly impact human health, based on drinking water consumption or other routes of exposure (e.g., inhalation, ingestion of food residues, dermal uptake). Primary ground water standards are enforceable ground water standards, not screening tools or guidance levels. To evaluate the potential impacts on aquatic life, due to the pulsed nature of exposure, the maximum observed concentration is compared to the Criterion Maximum Concentration published by the USEPA under Section 304

(a) of the Clean Water Act, if available, or the lowest EC₅₀ or LC₅₀ reported in the summarized literature. Sediment concentrations are compared to freshwater sediment quality assessment guidelines (MacDonald Environmental Sciences, LTD., and United States Geological Survey (2003). A value below the threshold effects concentration (TEC) should not have a harmful effect on sediment-dwelling organisms. Values above the probable effect concentration (PEC) demonstrate harmful effects on sediment-dwelling organisms are likely to be frequently or always observed. This summary covers surface water and sediment samples collected from May 11 to May 14, 2003.

Results

At least one pesticide was detected in surface water at 32 of the 39 sites and in sediment at 15 of the 35 sites. Sediment samples are not routinely collected at GORDYRD, CR33.5T, NSIDWC06, and NSIDWC07. The concentrations of the pesticides detected at each of the sites are summarized for the surface water and sediment in Tables 2 and 3, respectively. All of these compounds have previously been detected in this monitoring program.

One DDD and four DDE compound sediment concentrations were of a magnitude considered to represent detrimental effects to sediment-dwelling organisms in freshwater sediments.

The above findings must be considered with the caveat that pesticide concentrations in surface water and sediment may vary significantly in relation to the timing and magnitude of pesticide application, rainfall events, pumping and other factors, and that this was only one sampling event. The possible long term or chronic toxicity impacts are also reported based on the single sampling event and do not take into account previous monitoring data.

Usage and Water Quality Impacts

2.4-D: 2,4-D is a selective systemic herbicide used for the post-emergence control of annual and perennial broad leaf weeds in terrestrial (grassland, established turf, sugarcane, rice, and on non-crop areas) as well as aquatic areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that 2,4-D (1) has minimum loss from soil by surface adsorption, with a moderate loss by leaching and surface solution; (2) is slightly toxic to mammals and relatively non-toxic to fish; and (3) does not bioaccumulate significantly. The highest 2,4-D concentration was detected at S18C (1.7 μ g/L) (Table 2). Using these criteria, these levels should not have an acute impact on fish or aquatic invertebrates.

Ametryn: Ametryn is a selective terrestrial herbicide registered for use on sugarcane, bananas, pineapple, citrus, corn, and non-crop areas. Most algal effects occur at concentrations > $10 \mu g/L$ (Verschueren, 1983). Environmental fate and toxicity data in Tables 4 and 5 indicate that ametryn (1) is lost from soil relatively easily by leaching, surface adsorption, and in surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data includes a 96 hour LC_{50} of 14.1 mg/L for goldfish (Hartley and Kidd, 1987). The ametryn surface water concentrations found in this sampling event ranged from 0.0098 to 0.065 μ g/L. Using these criteria, these surface water levels should not have an acute, detrimental impact on fish or aquatic invertebrates. The sediment concentrations ranged from 6.8 to 35 μ g/Kg. However, no freshwater sediment quality

assessment guidelines have been developed for ametryn.

Atrazine: Atrazine is a selective systemic herbicide registered for use on pineapple, sugarcane, corn, rangelands, ornamental turf and lawn grasses, and non-crop areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that atrazine (1) is easily lost from soil by leaching and in surface solution, with moderate loss from surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96 hour LC₅₀ of 76 mg/L for carp, 16 mg/L for perch and 4.3 mg/L for guppies (Hartley and Kidd, 1987). Also, in a flow-through bioassay, the maximum acceptable toxicant concentration (MATC) of atrazine was 90 and 210 μ g/L for bluegill and fathead minnow (Verschueren, 1983). The atrazine surface water concentrations found in this sampling event at 24 of the 39 sampling locations, ranged from 0.011 to 3.8 μ g/L. Using these criteria, these surface water levels should not have an acute or chronic detrimental impact on fish or invertebrates. Atrazine was quantified in the sediment at 6.2 μ g/Kg at S7. Only a TEC (0.30 μ g/Kg) was established for atrazine. It is uncertain if detrimental impacts will occur to bottom-dwelling organisms.

Atrazine desethyl (DEA) and atrazine desisopropyl (DIA) are biotic degradation products of atrazine. These degradation products are both persistent and mobile in water; however, DEA is more stable and the dominant initial metabolite. Since DEA and DIA are structurally and toxicologically similar to atrazine, the concentrations of total atrazine residue (atrazine + DEA + DIA) may also be a significant consideration in the surface water environment. The DEA to atrazine ratio (DAR), on a molar basis, has been suggested as an indicator of nonpoint-source pollution of groundwater (Adams and Thurman, 1991) and as a tracer of ground water discharge into rivers (Thurman et al., 1992). Goolsby et al. (1997) determined that low DAR values, median <0.1, occur in streams during runoff shortly after application of atrazine. Higher DAR values, median about 0.4, occur later in the year after considerable degradation of atrazine to DEA has occurred in the soil. The low median DAR ratio (0.1) at the locations where both atrazine and DEA were detected, suggests minimum degradation of atrazine (Table 6). Most of the sites fall in this category with the exception of S3. The DAR value of 0.3 suggests that some degradation of atrazine has occurred in this basin. However, these general guidelines were developed based on observations in Midwest watersheds in northern temperate climates with different soil and water management regimes as well as higher atrazine water concentrations. Applications to the south Florida environment should be made with caution.

Bromacil: Bromacil is a terrestrial herbicide registered for use on pineapple, citrus, and non-crop areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that bromacil (1) is easily lost from soil by leaching, with moderate loss from surface adsorption or surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data includes a 96 hour LC₅₀ of 164 mg/L for carp (Hartley and Kidd, 1987). The highest concentration of bromacil detected in the surface water during this sampling event was at S79 (0.16 μ g/L). Using these criteria, these levels should not have an acute or chronic detrimental impact on fish. Bromacil was not quantified in the sediment.

<u>DDD</u>, <u>DDE</u>, <u>DDT</u>: DDE is an abbreviation of **d**ichloro**d**iphenyldichloro**e**thylene [2,2-bis(4-chlorophenyl)-1,1-dichloroethene]. DDE is an environmental dehydrochlorination product of DDT (**d**ichloro**d**iphenyltrichloroethane), a popular insecticide for which the USEPA cancelled all uses in 1973. The large volume of DDT used, the persistence of DDT, DDE and another metabolite, DDD (**d**ichloro**d**iphenyl**d**ichloroethane), and the high K_{oc} of these compounds accounts for the frequent detections in sediments. The large hydrophobicity of these compounds also results in a significant bioaccumulation factor (Table 4). In sufficient quantities, these residues have reproductive effects in wildlife and carcinogenic effects in many mammals.

The DDD concentrations detected range from 1.2 to 34 $\mu g/Kg$. Any concentration below the TEC (4.9 $\mu g/Kg$) should not impact sediment dwelling organisms while concentrations above the PEC (28 $\mu g/Kg$), frequently or always have the possibility for impacting sediment-dwelling organisms. The sediment concentration detected at S5A (34 $\mu g/Kg$) exceeds the PEC.

The TEC is $3.2 \mu g/Kg$ and the PEC is $31 \mu g/Kg$ for DDE in freshwater sediments. The concentrations of DDE detected at S178, S2, S5A, and S6 exceed the PEC and frequently or always have the possibility for impacting sediment-dwelling organisms.

One of the DDT concentration's detected (5.3 μ g/Kg at S3) exceeds the TEC (4.2 μ g/Kg) but is less than the PEC (63 μ g/Kg). It is uncertain if this level will have the possibility for impacting sediment-dwelling freshwater organisms.

<u>Diuron</u>: Diuron is a selective, systemic terrestrial herbicide registered for use on sugarcane, bananas, and citrus. Environmental fate and toxicity data in Tables 4 and 5 indicate that diuron (1) is easily lost from soil in surface solution, with moderate loss from leaching or surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data includes a 96-hour LC₅₀ of 25 mg/L for guppies (Hartley and Kidd, 1987). Crustaceans are affected at lower concentrations with a 48 hour LC₅₀ of 1.4 mg/L for water fleas and a 96 hour LC₅₀ of 0.7 mg/L for water shrimp (Verschueren, 1983). Most algal effects occur at concentrations > 10 μg/L (Verschueren, 1983). The only surface water concentration of diuron found during this sampling event was 0.33 μg/L (Table 2). Using these criteria, this level should not have an acute, harmful impact on fish or algae. Diuron was not detected in the sediment.

Ethion: Ethion is a non-systemic acaricide and insecticide registered for use on several fruits, citrus, and vegetables. The use of ethion on citrus has been cancelled (Federal Register, March 22, 2002). By December 31, 2004, all use of existing stocks of the end-use products is prohibited. Environmental fate and toxicity data in Tables 4 and 5 indicate that ethion (1) is strongly sorbed to soil and therefore can accumulate in sediments; (2) is slightly toxic to mammals, relatively toxic to fish and extremely toxic to Daphnia; and (3) bioconcentrates to a limited extent. Several sources of toxicity information have shown both agreement and disagreement of these laboratory tests. Ethion was only detected in the sediment at S99 (3.0 μg/Kg). The last sediment ethion detection at this site occurred during the June 2002 sampling event. However, no sediment quality assessment guidelines have been developed for ethion.

Endosulfan sulfate: Endosulfan sulfate is an oxidation metabolite of the insecticide endosulfan. The water solubility and Henry's constant indicate that endosulfan sulfate is less volatile than water and concentrations will increase as water evaporates (Lyman et al., 1990). Endosulfan sulfate has a relatively high degree of accumulation in aquatic organisms (Table 4). The only surface water detection occurred at S178 (0.047 μ g/L). However, no FDEP surface water standard (FAC 62-302) has been promulgated for endosulfan sulfate.

Hexazinone: Hexazinone is a non-selective contact herbicide that inhibits photosynthesis. Registered uses include sugarcane, pineapple, and non-crop areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that hexazinone (1) is easily lost from soil by leaching, with moderate loss from surface adsorption or surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Hexazinone is practically non-toxic to freshwater invertebrates with an EC₅₀ of 145 mg/l for *Daphnia magna* (U.S. Environmental Protection Agency, 1988). The highest surface water concentration detected in this sampling event at FECSR78 (0.079 μ g/L) should not have an acute impact on fish or aquatic invertebrates

Metolachlor: Metolachlor is a selective herbicide used on potatoes, sugarcane, and some vegetables. Environmental fate and toxicity data in Tables 4 and 5 indicate that metolachlor (1) has a large potential for loss due to leaching and a medium potential for loss in surface solution and due to surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Metolachlor is non-toxic to birds (Lyman et al., 1990). The only surface water concentration found in this sampling event (0.14 μ g/L at S78) is over two orders of magnitude below the calculated chronic action level. Using these criteria, these levels should not have a harmful impact on fish or aquatic invertebrates.

Norflurazon: Norflurazon is a selective herbicide registered for use on many crops including citrus. Environmental fate and toxicity data in Tables 4 and 5 indicate that norflurazon (1) is easily lost from soil surface solution and a moderate potential for loss due to leaching and surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. The LC₅₀ for norflurazon is >200 mg/L for catfish and goldfish (Hartley and Kidd, 1987). The norflurazon surface water concentrations ranged from 0.027 to 0.60 μ g/L. Even at the highest concentration, this is over an order of magnitude below the calculated chronic action level. Using these criteria, these levels should not have an acute, detrimental impact on fish or aquatic invertebrates.

<u>PCBs</u>: Polychlorinated biphenyls (PCBs) is the generic term for a group of 209 congeners that contain a varying number of substituted chlorine atoms on one or both of the biphenyl rings. PCB-1254 is a commercial grade mixture containing 54% chlorine by weight. Production of PCBs was banned in 1978 and closed system uses are being phased out. In natural water systems, PCBs are found primarily sorbed to suspended sediments due to the very low solubility in water (Callahan et al., 1979). The tendency of PCBs for adsorption increases with the degree of chlorination and with the organic content of the adsorbent. While the production ban, phase out of uses, and stringent spill clean-up requirements have significantly reduced environmental loadings in recent years, the persistence and tendency to accumulate in sediment and

bioaccumulate in fish, make this class of organochlorine compounds especially problematic. The Florida freshwater sediment quality assessment guidelines have been developed for total PCBs (MacDonald Environmental Sciences, LTD., and United States Geological Survey, 2003). The TEC and PEC is $60~\mu g/Kg$ and $680~\mu g/Kg$, respectively, for total PCB's. The sediment residues detected all fall between the TEC and PEC, which therefore have a possibility for impacting freshwater sediment-dwelling organisms. None of the PCB congeners were detected in the surface water.

<u>Prometon</u>: Prometon is a non-selective systemic herbicide registered for use in non-crop areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that prometon (1) is easily lost from soil by leaching, with moderate loss from surface adsorption or surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. The highest concentration of prometon detected (0.054 μ g/L at NSIDC07) is several orders of magnitude below the calculated chronic action level. Using these criteria, these levels should not have an acute, detrimental impact on fish or aquatic invertebrates. Prometon was not detected in the sediment

Simazine: Simazine is a selective systemic herbicide registered for use on many crops including sugarcane, citrus, corn, and non-crop areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that simazine (1) is easily lost from soil by leaching and has a moderate potential for loss due to surface adsorption and surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96 hour LC₅₀ of 49 mg/L for guppies (Hartley and Kidd, 1987). Most of the aquatic biological effects occur at concentrations > 500 μ g/L (Verschueren, 1983). Aquatic invertebrate LC₅₀ toxicity ranges from 3.2 mg/L to 100 mg/L for simazine (U.S. Environmental Protection Agency, 1984). The highest surface water concentration of simazine detected at G94D (0.43 μ g/L) was below any level of concern for fish or aquatic invertebrates. No simazine was detected in the sediment.

Quality Assurance Evaluation

Replicate samples were collected at sites S355B, and S79. All the analytes detected in the surface water had precision \leq 30% RPD. No analytes were detected in the field blanks collected at S332, S4, S6, S7, and S9. No pesticide analytes were detected in the equipment blanks performed at S18C, S142, and S99. All collected samples were shipped and all bottles were received.

Low concentrations of representative analytes from each pesticide group/method were added to laboratory water as well as to samples submitted Matrix spike recoveries for parathion ethyl did not meet the specified requirements for the water samples collected at the following locations: S355A, S355B (including replicates), S12C, US4125, S18C, S178, S177, S332 (including field blank), S176, and S331. The remainder of the analytes for each sample adhered to the targets for precision and accuracy as outlined in the FDEP Comprehensive Quality Assurance Plan. Organic quality assurance targets are set according to historically generated data or are adapted from the U.S. Environmental Protection Agency with slight modifications or internal goals,

based on FDEP limited data. Parameters with low or high recoveries indicate that the sample matrix interferes with these analyses and interpretation of the respective analytical results should consider this effect.

Glossary

- LD₅₀: The dosage which is lethal to 50% of the terrestrial animals tested within a short (acute) exposure period, usually 24 to 96 hours.
- LC₅₀: A concentration which is lethal to 50% of the aquatic animals tested within a short (acute) exposure period, usually 24 to 96 hours.
- EC₅₀: A concentration necessary for 50% of the aquatic species tested to exhibit a toxic effect short of mortality (e.g., swimming on side or upside down, cessation of swimming) within a short (acute) exposure period, usually 24 to 96 hours.
- Koc: The soil/sediment partition or sorption coefficient normalized to the fraction of organic carbon in the soil. This value provides an indication of the chemical's tendency to partition between soil organic carbon and water.

Bioconcentration Factor:

The ratio of the concentration of a contaminant in an aquatic organism to the concentration in water, after a specified period of exposure via water only. The duration of exposure should be sufficient to achieve a near steady-state condition.

Soil or water half-life:

The time required for one-half the concentration of the compound to be lost from the water or soil under the conditions of the test.

- MDL: The minimum concentration of an analyte that can be detected with 99% confidence of its presence in the sample matrix.
- PQL: The lowest level of quantitation that can be reliably achieved within specified limit of precision and accuracy during routine laboratory operating conditions. The PQL is further verified by analyzing spike concentrations whose relative standard deviation in 20 fortified water samples is < 15%. In general, the PQL is 2 to 5 times larger than the MDL.
- TEC: The threshold effects concentration is intended to identify concentrations below which harmful effects on freshwater sediment-dwelling organisms are unlikely to be observed.
- PEC: The probable effects concentration is intended to identify concentrations above which harmful effects on sediment-dwelling organisms are likely to be frequently or always observed.

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Figure 1. South Florida Water Management District Pesticide Monitoring Network.

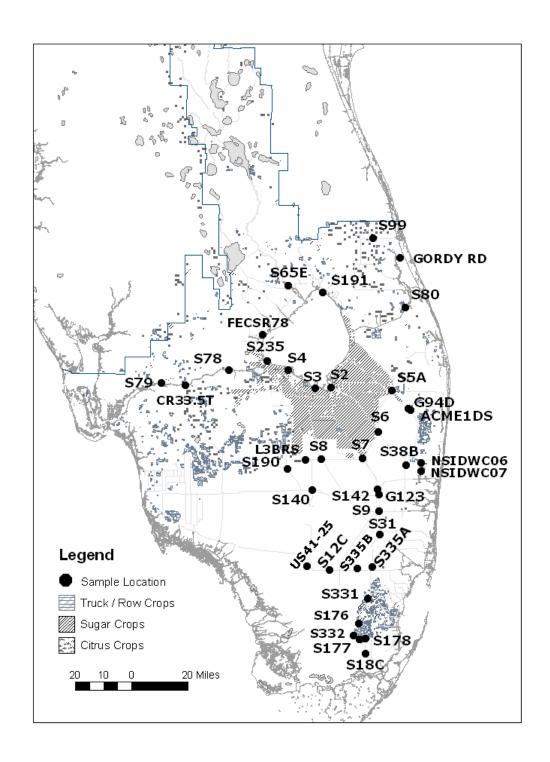


Table 1. Minimum detection limits (MDL) and preactial quantitation limits (PQL) for pesticides determined in May 2003.

Pesticide or metabolite	Water: range of MDL-PQL (µg/L)	Sediment: range of MDL - PQL (µg/Kg)	Pesticide or metabolite	Water: range of MDL-PQL (µg/L)	Sediment: range of MDL - PQL (µg/Kg)
2,4-D	0.2 - 140	8.3 - 200	endosulfan sulfate	0.0045 - 0.2	0.83 - 26.8
2,4,5-T	0.2 - 140	8.3 - 200	endrin	0.019 - 0.2	1.6 - 52
2,4,5-TP (silvex)	0.2 - 140	8.3 - 200	endrin aldehyde	0.0042 - 0.08	0.83 - 26.8
alachlor	0.047 - 2.4	25 - 800	ethion	0.019 - 0.2	2.1 - 68
aldrin	0.0019 - 0.04	0.41 - 13.2	ethoprop	0.019 - 0.4	4.1 - 132
ametryn	0.0094 - 0.2	2.1 - 68	fenamiphos (nemacur)	0.028 - 0.8	16 - 520
atrazine	0.0094 - 0.384	2.1 - 68	fonofos (dyfonate)	0.019 - 0.4	4.1 - 132
atrazine desethyl	0.0094 - 0.0392	N/A	heptachlor	0.0023 - 0.04	0.41 - 13.2
atrazine desisopropyl	0.0094 - 0.0392	N/A	heptachlor epoxide	0.0019 - 0.08	0.41 - 13.2
azinphos methyl (guthion)	0.019 - 0.2	2.1 - 68	hexazinone	0.019 - 0.4	8.3 - 268
α-BHC (alpha)	0.0021 - 0.04	0.41 - 16	imidacloprid	0.2 - 140	8.3 - 200
β-BHC (beta)	0.0032 - 0.04	0.41 - 13.2	linuron	0.2 - 140	8.3 - 200
δ-BHC (delta)	0.0019 - 0.04	0.83 - 26.8	malathion	0.028 - 0.6	6.2 - 200
γ-BHC (gamma) (lindane)	0.0019 - 0.04	0.41 - 13.2	metalaxyl	0.047 - 0.196	N/A
bromacil	0.038 - 0.8	16 - 520	methamidophos	N/A	21 - 680
butylate	0.019 - 0.08	N/A	methoxychlor	0.0098 - 0.2	2.1 - 68
carbophenothion (trithion)	0.015 - 0.12	2.1 - 68	metolachlor	0.057 - 2	21 - 680
chlordane	0.019 - 0.8	6.2 - 200	metribuzin	0.019 - 0.4	4.1 - 132
chlorothalonil	0.015 - 0.16	2.1 - 68	mevinphos	0.057 - 0.8	8.3 - 268
chlorpyrifos ethyl	0.019 - 0.2	2.1 - 68	mirex	0.011 - 0.08	1.6 - 52
chlorpyrifos methyl	0.0094 - 0.4	4.1 - 132	monocrotophos (azodrin)	N/A	41 - 1320
cypermethrin	0.019 - 0.2	2.1 - 68	naled	0.075 - 3.2	33 - 1080
DDD-P,P'	0.0045 - 0.08	0.83 - 26.8	norflurazon	0.019 - 0.4	4.1 - 132
DDE-P,P'	0.0038 - 0.08	0.83 - 26.8	parathion ethyl	0.019 - 0.6	6.2 - 200
DDT-P,P'	0.0038 - 0.12	1.2 - 40	parathion methyl	0.019 - 0.4	6.2 - 200
demeton	0.11 - 4	41 - 1320	PCB	0.019 - 1.2	8.7 - 600
diazinon	0.019 - 0.2	4.1 - 132	permethrin	0.015 - 0.24	2.5 - 80
dicofol (kelthane)	0.042 - 0.6	6.2 - 200	phorate	0.028 - 0.2	2.1 - 68
dieldrin	0.0019 - 0.08	0.41 - 13.2	prometryn	0.019 - 0.6	6.2 - 200
disulfoton	0.019 - 0.4	4.1 - 132	prometon	0.019 - 0.08	N/A
diuron	0.2 - 140	8.3 - 200	simazine	0.0094 - 0.2	2.1 - 68
α-endosulfan (alpha)	0.0038 - 0.08	0.41 - 13.2	toxaphene	0.094 - 3	31 - 1000
β-endosulfan (beta)	0.0038 - 0.08	0.41 - 13.2	trifluralin	0.0075 - 0.16	1.6 - 52

N/A - not analyzed

Table 2. Summary of pesticide residues ($\mu_{g/L}$) above the method detection limit found in surface water samples collected by SFWMD in May 2003.

Date	Site	Flow	2,4-D	ametryn	atrazine	atrazine desethyl	atrazine desisopropyl	bromacil	diuron	endosulfan sulfate	hexazinone	metolachlor	norflurazon	prometon	simazine	Number of compounds detected at site
5/11/2003	S176	N	-	-	0.056	-	-	-	-	-	-	-	-	-	-	1
	S177	N	0.61	-	0.024 I	-	-	-	-	-	-	-	-	-	-	2
	S178	N	0.53 I	-	-	-	-	-	-	0.047	-	-	-	-	-	2
	S18C	N	1.7	-	0.019 I	-	-	-	-	-	-	-	-	-	-	2
	S331	Υ	-	-	0.22	0.026 I	-	-	-	-	-	-	-	-	-	2
	S332	N	-	-	0.018 I	-	-	-	-	-	-	-	-	-	-	1
5/12/2003	G123	N	-	-	0.23	-	-	-	-	-	-	-	-	-	-	1
	S12C	N	-	-	0.021 I	-	-	-	-	-	-	-	-	-	-	1
	S31	N	-	-	-	-	-	-	-	-	-	-	-	-	-	0
	S355A	N	-	-	0.011 I	-	-	-	-	-	-	-	-	-	-	1
	S355B	N	-	-	0.039 I*	-	-	-	-	-	-	-	-	-	-	1
	S9	N	-	-	-	-	-	-	-	-	-	-	-	-	-	0
	US41-25	N	-	-	-	-	-	-	-	-	-	-	-	-	-	0
5/13/2003	C25S99	N	-	-	-	-	0.012 I	0.061 I	-	-	-	-	0.60	-	0.056	4
	GORDYRD	Υ	-	-	-	-	-	0.054 I	-	-	-	-	-	-	0.027 I	2
	L3BRS	N	-	0.033 I	0.60	0.052	0.017 I	-	-	-	-	-	-	-	-	4
	S140	N	-	-	0.069	0.011 I	-	-	-	-	-	-	0.049 I	-	-	3
	S142	N	-	0.025 I	0.040	-	-	-	-	-	-	-	-	-	-	2
	S190	N	-	-	0.047	-	-	-	-	-	-	-	0.044 I	-	0.037 I	3
	S2	N	-	-	0.28	0.039	0.011 I	-	-	-	-	-	-	-	0.011 I	4
	S3	N	-	-	0.32	0.044	0.015 I	-	-	-	-	-	-	-	-	3
	S4	N	-	0.015 I	0.37	0.036 I	0.012 I	-	-	-	-	-	0.027 I	-	-	5
	S7	Υ	-	0.020 I	0.28	0.019 I	-	-	-	-	-	-	-	-	-	3
	S8	N	-	0.029 I	0.71	0.067	0.016 I	-	-	-	-	-	-	-	-	4
	S80	Υ	-	-	0.21	0.032 I	0.010 I	-	-	-	-	-	0.11	-	0.013 I	5
5/14/2003	ACME1DS	N	-	0.071	1.3	0.082	0.024 I	-	-	-	0.022 I	-	-	-	0.30	6
	CR33.5T	R	-	0.012 I	0.86	0.056	0.017 I	0.068 I	-	-	-	-	0.13	-	0.068	7
	FECSR78	N	-	-	0.046	-	-	-	-	-	0.079	-	-	-	-	2
	G94D	N	-	0.065	1.5	0.089	0.029 I	-	-	-	-	-	-	-	0.43	5
	NSIDWC06	N	-	0.012 I	1.4	0.14	0.026 I		0.33 I	-	-	-	-	-		5
	NSIDWC07	N	-	0.024 I	3.8	0.32	0.045	-	-	-	-	-	-	0.054 I	0.011 I	6
	S191	N	-	-	0.045	-	-	0.14 I	-	-	-	-	-	-	-	2
	S235	R	-					-	-	-	-	-	-		-	0
	S38B	N	-	0.012 I	2.1	0.17	0.027 I	-	-	-	-	-	-	0.033 I	-	5
	S5A	Y	-	- 0.007.1	0.23	0.029 I	-	-	-	-	-	-	-	-	0.014 I	3
	S6	Y	-	0.037 I	0.47	0.039	0.014 I	-	-	-	-	-	-	-	0.015 I	5
	S65E	Y	0.37 I		0.18	0.018 I	-	-	-	-	-	-	-	-	-	3
	S78	Y	-	0.0098 I	0.47	0.041	0.015 I		-	-	- 0.004.16	0.14 I	0.040 I	-	0.012 I	7
	S79	Υ	-	0.018 I*	2.3 *	0.097 *	0.022 *	0.16 *	-	-	0.024 *	-	0.18 *	-	0.081 *	8
Total number of	f compound dete			14	32	20	16	5	1	1	3	1	8	2	13	120

N - no Y - yes R - reverse; - denotes that the result is below the MDL; * results are the average of replicate samples I - value reported is less than the minimum quantitative limit, and greater than or equal to the minimum detection limit.

Table 3. Summary of pesticide residues (µg/Kg) above the method detection limit found in sediment samples collected by SFWMD in May 2003.

Date	Site	Flow	ametryn	atrazine	DDD-P,P'	DDE-P,P'	DDT-P,P'	ethion	norflurazon	PCB-1254	Number of compounds detected at site
5/11/2003	S177	N	-	-	-	3.2 I	-	-	-	-	1
Ī	S178	N	-	-	-	38	-	-	-	-	1
	S18C	N	-	-	-	1.9 I	-	-	-	-	1
5/12/2003	S31	N	-	-	-	3.0 I	-	-	-	-	1
	S9	N	-	-	-	2.2	-	-	-	-	1
5/13/2003	C25S99	N	-	-	-	-	-	3.0 I	6.2 I	-	2
	S142	N	-	-	3.1 I	13	-	-	-	-	2
Ī	S2	N	14 I	-	13 I	52	-	-	-	-	3
	S3	N	-	-	5.3 I	14	5.3 I	-	-	-	3
Ī	S4	N	35 I	-	-	22 I	-	-	-	82 I	3
Ī	S7	Υ	-	6.2 I	-	-	-	-	-	470	2
	S80	Υ	-	-	-	5.3 I	-	-	i	58 I	2
5/14/2003	ACME1DS	N	-	-	1.2 I	3.6 I	-	-	-	-	2
Ī	G94D	N	-	-	-	2.5 I	1.8 I	-	-	-	2
Ī	S5A	Υ	18 I	-	34	84	-	-	-	160 I	4
Ī	S6	Υ	6.8 I	-	17	42	-	-	-	-	3
	S79	Υ	-	-	-	7.7 l	-	-	-	145 I*	2
Total number o	of compound dete	ctions	4	1	6	15	2	1	1	5	35

N - no Y - yes R - reverse; - denotes that the result is below the MDL; * results are the average of replicate samples

I - value reported is less than the minimum quantitative limit, and greater than or equal to the minimum detection limit.

Table 4. Selected properties of pesticides found in May 2003 sampling event.

Tubio ii odiodiou	Surface	Ground	LD50								
					18/-4		9				
	Water	Water	acute rats		Water		soil				
	Standards	Guidance	oral	EPA	Solubility	Koc	half-life				
	62-302	Conc.	(mg/kg)	carcinogenic	(mg/L)	(mL/g)	(days)	SC	S ratin	g (2)	Bioconcentration
common name	(µg/L)	(μg/L)	(1)	potential	(2, 3)	(2, 3)	(2, 3)	LE	SA	SS	Factor (BCF)
2,4-D (acid)	(100)	70**	375	D	890	20	10	М	S	M	13
ametryn	-	63	1110	D	185	300	60	М	M	M	33
atrazine	-	3**	3080	С	33	100	60	L	M	L	86
bromacil	-	90	5200	С	700	32	60	L	M	M	15
DDD, p,p'	-	0.1	3400	-	0.055	239900	-	-	-	-	3173
DDE, p,p'	-	0.1	880	-	0.065	243220	-	-	-	-	2887
DDT, p,p'	0.001	0.1	113	-	0.00335	140000	-	-	-	-	15377
diuron	-	14	3400	D	42	480	90	М	M	L	75
endosulfan sulfate	-	0.3	-	-	0.117	-	-	-	-	-	2073
ethion	-	3.5	208	-	1.1	8900	150	S	L	M	586
hexazinone	-	231	1690	D	33000	54	90	L	M	M	2
metolachlor	-	1050	2780	С	530	200	90	L	M	M	18
norflurazon	-	280	9400	С	28	700	90	М	М	L	94
PCB's	0.014	0.5**	-	B2	_	-	-	-	-	-	-
prometon	-	105	2980	-	720	200	500	L	М	М	15
simazine	-	4**	>5000	С	6.2	130	60	L	M	М	221

SCS Ratings are pesticide loss due to leaching (LE), surface adsorption (SA) or surface solution (SS) and grouped as large(L), medium (M), small (S) or extra small (XS) Bioconcentration Factor (BCF) calculated as BCF = $10^{\circ}(2.791 - 0.564 \log WS)$ (4)

B2: probable human carcinogen; C: possible human carcinogen; D: not classified; E: evidence of non-carcinogen for humans (5)

FDEP surface water standards for Class III waters except Class I in ()

- (1) Hartley, D. and H. Kidd. (Eds.) (1987).
- (2) Goss, D. and R. Wauchope. (Eds.) (1992).
- (3) Montgomery, J.H. (1993).
- (4) Lyman, W.J., W.F. Reehl, and D.H. Rosenblatt. (1990).
- (5) U.S. Environmental Protection Agency (1996).

^{**} primary standard

Table 5. Toxicity of pesticides found in the May 2003 sampling event to freshwater aquatic invertebrates and fishes (ug/L).

	. <u> </u>	<u> </u>											o iniverted											
	48 hr EC	50			96 hr LC	50			96 hr LC	50			96 hr LC5	50			96 hr LC5	0			96 hr LC5	50	}	
common name	Water fl	ea	acute	chronic	Fathea Minnow				Bluegill				Largemou Bass	ıth			Rainbow Trou	ut (#)			Channel Ca	ıtfish		
Hame	Daphni	а	toxicity	toxicity	Pimepha	les	acute	chronic	Lepomis	S	acute	chronic	Micropter	ıs	acute	chronic	Oncorhynch	ius	acute	chronic	Ictalurus	3	acute	chronic
	magna	7	(*)	(*)	promela	s	toxicity	toxicity	macrochii	นร	toxicity	toxicity	salmoide	s	toxicity	toxicity	mykiss		toxicity	toxicity	punctatu	s	toxicity	toxicity
2,4-D	25,000	(8)	8333	1250	133,000	(8)	44333	6650	180,000	(9)	60000	9000	-		-	-	100,000	(5)	33333	5000	-		-	-
	-			-	-		-	-	900 (48 hr)	(7)	-	-	-		-	-	110,000	(8)	36667	5500	-		-	-
ametryn	28,000	(8)	9333	1400	-		-	-	4,100	(5)	1367	205	-		-	-	8,800	(5)	2933	440	-		-	-
atrazine	6900	(8)	2300	345	15,000	(8)	5000	750	16,000	(5)	5333	800	-		-	-	8,800	(5)	2933	440	7,600	(5)	2533	380
bromacil	-		-	-	-		-	-	127,000	(8)	42333	6350	-		-	-	36,000	(8)	12000	1800	-		-	-
DDD, p,p'	3,200	(7)	1067	160	4,400	(1)	1467	220	42	(1)	14	2.1	42	(1)	14	2.1	70	(1)	23.3	3.5	1,500	(1)	500	75
DDE, p,p'	-		-	-	-		-	-	240	(1)	80	12	-			ı	32	(1)	10.7	1.6	-		-	-
DDT, p,p'	-		-	-	19	(6)	6.3	0.95	8	(6)	2.7	0.4	2	(6)	0.7	0.10	7	(6)	2.3	0.35	16	(6)	5.3	8.0
diuron	1,400	(8)	467	70	14,200	(8)	4733	710	5,900	(5)	1967	295	-		-	-	5,600	(5)	1867	280	-		-	-
endosulfan	166	(8)	55	8	1	(1)	0.3	0.05	1	(1)	0.33	0.05	-		-	-	1	(1)	0.33	0.050	1	(1)	0.3	0.05
	-		-	-	-		-	-	2	(3)	0.67	0.10	-		-	-	3	(2)	1	0.15	1.5	(8)	0.5	0.08
	-		-	-	-		-	-	-		-	-	-		•	-	1	(3)	0.33	0.050	-		-	-
	-		-	-	-		-	-	-		-	-	-		-	1	0.3	(6)	0.10	0.015	-		-	-
ethion	0.06	(1)	0.02	0.003	720	(1)	240	36	210	(1)	70	11	173	(1)	58	9	500	(1)	167	25	7,600	(1)	2533	380
	-		-	-	-		-	-	13	(3)	4.3	0.65	150	(4)	50	8	193	(3)	64	10	7,500	(4)	2500	375
	-		-	-	-		-	-	22	(4)	7.3	1.1	-				560	(4)	187	28	-		-	-
hexazinone	151,600	(8)	50533	7580	274,000	(5)	91333	13700	100,000	(8)	33333	5000	ı			ı	180,000	(8)	60000	9000	-		-	-
metolachlor	23,500	(8)	7833	1175	-		-	-	15,000	(5)	5000	750	-		-	1	2,000	(5)	667	100	4,900	(6)	1633	245
norflurazon	15,000	(8)	5000	750	-		-	-	16,300	(8)	5433	815	-		-	-	8,100	(8)	2700	405	>200,000	(5)	>67,000	>10,000
prometon	-		-	-	-		-	-	40,000	(6)	13333	2000	-		-	-	12,000	(6)	4000	600	-		-	-
simazine	1,100	(8)	367	55	100,000	(8)	33333	5000	90,000	(5)	30000	4500	-		-	-	100,000	(8)	33333	5000	-		-	-

^(*) Florida Administrative Code (FAC) 62-302.200, for compounds not specifically listed, acute and chronic toxicity standards are calculated as one-third and one-twentieth, respectively, of the amount lethal to 50% of the test organisms in 96 hours, where the 96 hour LC50 is the lowest value which has been determined for a species significant to the indigenous aquatic community.

- (1) Johnson, W. W. and M.T. Finley (1980).
- (2) U.S. Environmental Protection Agency (1977).
- (3) Schneider, B.A. (Ed.) (1979).
- (4) U.S. Environmental Protection Agency (1972).
- (5) Hartley, D. and H. Kidd. (Eds.) (1987).
- (6) Montgomery, J.H. (1993).
- (7) Verschueren, K. (1983).
- (8) U.S. Environmental Protection Agency (1991).
- (9) Mayer, F.L., and M.R. Ellersieck. (1986).

^(#) Species is not indigenous. Information is given for comparison purposes only.

Table 6. Atrazine Desethyl/Atrazine ratio data for May 2003.

			1			1	
Date	Site	Flow	atrazine		atrazine		
Bate	Oito		ug/l	moles/L	desethyl	moles/L	DAR
5/11/2003	S331	Υ	0.22	1.02E-09	0.026	1.39E-10	0.1
5/13/2003	L3BRS	N	0.60	2.78E-09	0.052	2.77E-10	0.1
	S140	N	0.069	3.20E-10	0.011	5.86E-11	0.2
	S2	N	0.28	1.30E-09	0.039	2.08E-10	0.2
	S3	N	0.32	1.48E-09	0.044	2.35E-10	0.2
	S4	N	0.37	1.72E-09	0.036	1.92E-10	0.1
	S7	Υ	0.28	1.30E-09	0.019	1.01E-10	0.1
	S8	N	0.71	3.29E-09	0.067	3.57E-10	0.1
	S80	Υ	0.21	9.74E-10	0.032	1.71E-10	0.2
5/14/2003	ACME1DS	N	1.3	6.03E-09	0.082	4.37E-10	0.1
	CR33.5T	R	0.86	3.99E-09	0.056	2.98E-10	0.1
	G94D	N	1.5	6.95E-09	0.089	4.74E-10	0.1
	NSIDWC06	N	1.4	6.49E-09	0.14	7.46E-10	0.1
	NSIDWC07	N	3.8	1.76E-08	0.32	1.71E-09	0.1
	S38B	N	2.1	9.74E-09	0.17	9.06E-10	0.1
	S5A	Υ	0.23	1.07E-09	0.029	1.55E-10	0.1
	S6	Υ	0.47	2.18E-09	0.039	2.08E-10	0.1
	S65E	Υ	0.18	8.35E-10	0.018	9.59E-11	0.1
	S78	Υ	0.47	2.18E-09	0.041	2.19E-10	0.1
	S79**	Υ	2.3	1.05E-08	0.097	5.15E-10	0.0
N - no flow	Y - flow: R -	reverse		DAR	All sites	Flow only sites	No flow sites

N - no flow; Y - flow; R - reverse

DAR	All sites	Flow only	No flow			
DAR	All Siles	sites	sites			
average	0.1	0.1	0.1			
median	0.1	0.1	0.1			
minimum	0.0	0.0	0.1			
maximum	0.2	0.2	0.2			

^{**} Average of the replicate samples